

Reaction of Dipyrrolidinoaluminum Hydride in Tetrahydrofuran with Selected Organic Compounds Containing Representative Functional Groups

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Received March 28, 1994

The approximate rates and stoichiometry of reaction of excess dipyrrolidinoaluminum hydride (DPAH) with selected organic compounds containing representative functional groups under standardized conditions (tetrahydrofuran, 0, reagent : compound = 4 : 1) were examined in order to define the characteristics of the reagent for selective reductions. The reducing ability of DPAH was also compared with that of bis(diethylamino)aluminum hydride (BEAH). The reagent appears to be stronger than BEAH, but weaker than the parent reagent in reducing strength. DPAH shows a unique reducing characteristics. Thus, the reagent reduces aldehydes, ketones, esters, acid chlorides, epoxides, and nitriles readily. In addition to that, α,β -unsaturated aldehyde is reduced to the saturated alcohol. Quinones are reduced cleanly to the corresponding 1,4-reduction products. The examination for possibility of achieving a partial reduction to aldehydes was also performed. Both primary and tertiary aromatic carboxamides are converted to aldehydes with a limiting amount of DPAH. Finally, disulfides and sulfoxides are readily reduced to thiols and sulfides, respectively.

Introduction

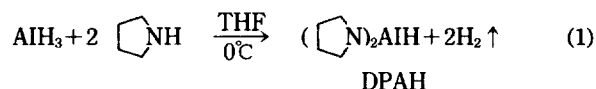
The addition of 2 moles of an amine to 1 mole of aluminum hydride provides a simple, convenient means of preparing derivatives which exhibit reducing properties significantly different from those of the parent reagent. For example, bis(*N*-methyl-piperazinyl)aluminum hydride has proven to be a valuable reagent for the selective reduction of carboxylic acids and esters to aldehydes.¹

A systematic survey of the characteristics of bis(diethylamino)aluminum hydride (BEAH),² one of the class of diethylamino derivatives, has revealed that it is a much milder reducing agent than the parent aluminum hydride.³

The addition of 2 moles of pyrrolidine, a cyclic secondary amine, at 0° produces dipyrrolidinoaluminum hydride. Preliminary observations indicated that the reducing potential of the pyrrolidino derivative lies somewhere between those of the diethylamino derivative and the parent reagent. Accordingly, it appeared desirable to undertake a systematic exploration of the reactions of dipyrrolidinoaluminum hydride with representative organic compounds, comprising the more common functional groups, in order to define the area of its probable utility.

Results and Discussion

Preparation of Dipyrrolidinoaluminum Hydride (DPAH) in THF. The reagent, dipyrrolidinoaluminum hydride (DPAH), was readily prepared by reaction of aluminum hydride with 2 equiv of pyrrolidine in THF in 3 h at 0 (eq. 1). Even in the presence of excess amine at 0 DPAH did not show any further reaction. However, at room



temperature the third hydride readily participated in the reaction with excess pyrrolidine. The experimental results are summarized in Table 1.

Table 1. Reaction of Aluminum Hydride with Excess Pyrrolidine^a in Tetrahydrofuran^b

Amine	Temp., °C	Reaction time, h				
		0.5	1.0	3.0	6.0	12.0
Pyrrolidine	0	1.98	1.99	2.00	—	2.00
	25	2.94	2.98	3.00		

^aThree equivalents of the amine were used. ^bMmol of hydrogen evolved per mmol of aluminum hydride.

The reagent in THF showed a broad singlet at δ 132 ppm in an ²⁷Al NMR spectrum and a stretching absorption for Al-H around 1824 cm⁻¹ in an IR spectrum.

Alcohols, Phenols, Amines, and Thiols (Active Hydrogen Compounds). There is no discrimination in the rate of hydrogen evolution among alcohols examined: all the alcohols examined readily liberated hydrogen quantitatively within 0.5 h 0°. The thiols examined also evolved 1 equiv of hydrogen rapidly. On the other hand, *n*-hexylamine liberated only 1 equiv of hydrogen rapidly, with the second being evolved slowly. The results are summarized in Table 2.

The diethylamino derivative, BEAH, shows a similar trend toward active hydrogen compounds.² However, the rate of reaction of DPAH appears to be faster than that of BEAH, while the rate being slower than that of aluminum hydride.³

Aldehydes and Ketones. All of the saturated aldehydes and ketones examined utilized 1 equiv of hydride rapidly in 0.5 h to produce the corresponding alcohols. The rate of reaction was much faster than BEAH, approaching that of the parent reagent. Like BEAH, the reaction of cinnamaldehyde involved the double bond readily to afford hydrocinnamyl alcohol. This is a contrast to the case of aluminum hydride,³ which gives only cinnamyl alcohol. These results are summarized in Table 3.

The stereoselectivity of DPAH in the reduction of cyclic ketones is summarized and compared to those of aluminum hydride and BEAH in Table 4. The introduction of dialkyl-

Table 2. Reaction of Dipyrrolidinoaluminum Hydride with Representative 'Active Hydrogen Compounds' in Tetrahydrofuran at 0°C

Compound ^a	Time, h	Hydrogen evolved ^b	Hydride used ^b	Hydride used for reduction ^b
1-Hexanol	0.25	0.91	0.91	0.00
	0.5	1.00	1.00	0.00
Benzyl alcohol	0.25	1.01	1.01	0.00
	0.5	1.01	1.01	0.00
3-Hexanol	0.25	0.89	0.89	0.00
	0.5	1.00	1.00	0.00
3-Ethyl-3-pentanol	0.25	0.90	0.90	0.00
	0.5	0.99	0.99	0.00
Phenol	0.25	0.94	0.94	0.00
	0.5	1.00	1.00	0.00
<i>n</i> -Hexylamine	0.25	0.99	0.99	0.00
	3.0	1.57	1.57	0.00
	24.0	1.85	1.85	0.00
	48.0	1.99	1.99	0.00
1-Hexanethiol	0.25	0.94	0.94	0.00
	0.5	1.01	1.01	0.00
Benzenthion	0.25	0.95	0.95	0.00
	0.5	1.00	1.00	0.00

^a 10.0 mmol of compound was added to 40.0 mmol of the reagent (0.5 M in reagent and 0.125 M in compound). ^b Mmol per a mmol of compound.

Table 3. Reaction of Dipyrrolidinoaluminum Hydride with Representative Aldehydes and Ketones in Tetrahydrofuran at 0°C


Compound ^a	Time, h	Hydrogen evolved ^b	Hydride used ^b	Hydride used for reduction ^b
Caproaldehyde	0.25	0.01	0.90	0.89
	0.5	0.01	1.01	1.00
Benzaldehyde	0.25	0.00	0.91	0.91
	0.5	0.00	1.00	1.00
2-Heptanone	0.25	0.03	0.96	0.93
	0.5	0.03	1.04	1.01
Norcamphor	0.25	0.00	0.98	0.98
	0.5	0.00	1.00	1.00
Acetophenone	0.25	0.00	0.93	0.93
	0.5	0.00	0.98	0.98
	1.0	0.00	1.00	1.00
Benzophenone	0.25	0.00	0.96	0.96
	0.5	0.00	1.00	1.00
Cinnamaldehyde ^c	0.25	0.00	1.48	1.48
	0.5	0.00	1.65	1.65
	1.0	0.00	1.85	1.85
	6.0	0.00	1.99	1.99

^{a,b} See corresponding footnotes in Table 2, ^c Solution changed to yellow.

amino group to the parent aluminum hydride appears not to be significantly influential in stereoselectivity.

Quinones. Again, DPAH and BEAH show a similar

Table 4. Stereochemistry in the Reduction of Cyclic Ketones with Dipyrrolidinoaluminum Hydride in Tetrahydrofuran at 0°C

Compound	Less stable isomer, % ^{a,b}		
	AlH ₃ ^c	(Et ₂ N) ₂ AlH ^d	() ₂ AlH
Cyclohexanone			
2-methyl-	26	51	28
3-methyl-		31	36
4-methyl-		41	23
4- <i>tert</i> -butyl-	13	21	46
3,3,5-trimethyl-	88	88	85
Norcamphor	93	94	94
Camphor	90	83	88

^a Excess reagent utilized, ^b Quantitative yields of alcohols, ^c Data taken from ref. 3. ^d Data taken from ref. 2.

Table 5. Reaction of Dipyrrolidinoaluminum Hydride with Representative Quinones in Tetrahydrofuran at 0°C

Compound ^a	Time, h	Hydrogen evolved ^b	Hydride used ^b	Hydride used for reduction ^b
<i>p</i> -Benzoquinone ^{c,d}	0.25	0.00	1.36	1.36
	0.5	0.01	1.80	1.79
	1.0	0.01	1.85	1.84
	3.0	0.01	1.97	1.96
	6.0	0.01	2.01	2.00
Anthraquinone ^e	0.25	0.03	1.77	1.74
	0.5	0.03	1.85	1.82
	1.0	0.03	1.94	1.91
	3.0	0.03	2.02	1.99
	6.0	0.03	2.02	1.99

^{a,b} See corresponding footnotes in Table 2, ^c Batch reaction, ^d Dark precipitate formed, ^e Reverse addition; color changed into yellow.

trend in the reaction of quinones.² The reaction of *p*-benzoquinone and anthraquinone with DPAH readily utilized 2 equiv of hydride without evolution of hydrogen to proceed cleanly to the 1,4-reduction products, 1,4-dihydroxycyclohexadiene and 9,10-dihydro-9,10-anthracenediol, respectively.⁴ The reaction of *p*-benzoquinone with aluminum hydride proceeded to afford a 50 : 50 mixture of hydroquinone and 1,4-dihydroxycyclohexadiene, whereas anthraquinone was reduced cleanly to the 1,4-reduction product. These results are summarized in Table 5.

Carboxylic Acids and Acyl Derivatives. Carboxylic acids were reduced readily to the corresponding alcohols with rapid evolution of 1 equiv of hydrogen. Like BEAH,² the reagent shows a possibility for preparing aldehydes from carboxylic acids. A preliminary experiment revealed that DPAH in a limiting amount reduces benzoic acid to benzaldehyde in a yield of 85% at 0°. An extensive study for this promising reaction is being under way. Acetic anhydride utilized 4 equiv of hydride readily to be reduced to 2 moles of ethanol, whereas cyclic anhydrides utilized 2 equiv of hydride relatively fast and further hydride consumption was only slow. On the other hand, acid chlorides were reduced

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1-Hexanol	0.25	0.91	0.91	0.00
	0.5	1.00	1.00	0.00
Benzyl alcohol	0.25	1.01	1.01	0.00
	0.5	1.01	1.01	0.00
3-Hexanol	0.25	0.89	0.89	0.00
	0.5	1.00	1.00	0.00
3-Ethyl-3-pentanol	0.25	0.90	0.90	0.00
	0.5	0.99	0.99	0.00
Phenol	0.25	0.94	0.94	0.00
	0.5	1.00	1.00	0.00
<i>n</i> -Hexylamine	0.25	0.99	0.99	0.00
	3.0	1.57	1.57	0.00
	24.0	1.85	1.85	0.00
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
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Caproaldehyde	0.25	0.01	0.90	0.89
	0.5	0.01	1.01	1.00
Benzaldehyde	0.25	0.00	0.91	0.91
	0.5	0.00	1.00	1.00
2-Heptanone	0.25	0.03	0.96	0.93
	0.5	0.03	1.04	1.01
Norcamphor	0.25	0.00	0.98	0.98
	0.5	0.00	1.00	1.00
Acetophenone	0.25	0.00	0.93	0.93
	0.5	0.00	0.98	0.98
	1.0	0.00	1.00	1.00
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Table 6. Reaction of Dipyrrolidinoaluminum Hydride with Representative Carboxylic Acids and Acyl Derivatives in Tetrahydrofuran at 0°C

Compound ^a	Time, h	Hydrogen evolved ^b	Hydride used ^b	Hydride used for reduction ^b
Caproic acid	0.25	0.99	2.41	1.42
	0.5	1.00	2.61	1.61
	3.0	1.00	2.85	1.85
	6.0	1.00	2.98	1.98
	12.0	1.00	3.00	2.00
Benzoic acid	0.25	1.00	2.46	1.46
	0.5	1.00	2.80	1.80
	1.0	1.00	2.88	1.88
	3.0	1.00	3.00	2.00
Acetic anhydride ^c	0.25	0.00	2.03	2.03
	1.0	0.00	2.52	2.52
	6.0	0.00	3.51	3.51
	12.0	0.00	3.70	3.70
	24.0	0.00	3.99	3.99
Succinic anhydride ^{c,d}	0.25	0.02	1.52	1.50
	1.0	0.02	1.89	1.87
	6.0	0.02	2.52	2.50
	24.0	0.02	2.72	2.70
	72.0	0.02	3.00	2.98
Phthalic anhydride ^c	0.25	0.04	1.24	1.20
	3.0	0.04	1.66	1.62
	12.0	0.04	2.03	1.99
	24.0	0.04	2.04	2.00
	48.0	0.04	2.13	2.09
Caproyl chloride	0.25	0.00	1.81	1.81
	0.5	0.00	1.93	1.93
	1.0	0.00	1.99	1.99
Benzoyl chloride	0.25	0.00	1.94	1.94
	0.5	0.00	1.99	1.99
	1.0	0.00	2.00	2.00

^{a,b} See corresponding footnotes in Table 2, ^cHydride to compound=6:1, ^dSolution changed to yellow.

readily to the corresponding alcohols. BEAH also reduces carboxylic acids, anhydrides and acid chlorides in a rate slower than DPAH. Aluminum hydride reacts with these compounds with remarkable ease.³ These results are summarized in Table 6.

Esters and Lactones. Like the case of BEAH, DPAH reduced esters to the corresponding alcohols in 3-12 h at 0°. γ -Butyrolactone and phthalide were also readily reduced to the diols. The reaction of isopropenyl acetate utilized 2 equiv of hydride for reduction and further hydride utilization was very sluggish. This suggests that the reduction produces an ethanol moiety and an aluminum derivative of the enol form of acetone which is inert to reduction. The experimental results are summarized in Table 7.

Epoxides. All the epoxides examined were reduced readily to the alcohols in 6 h at 0°. The rate of reaction of this reagent is similar to that of BEAH² (Table 8). The reduction of 1,2-butylene oxide gives 87% 2- and 13% 1-bu-

Table 7. Reaction of Dipyrrolidinoaluminum Hydride with Representative Esters and Lactones in Tetrahydrofuran at 0°C

Compound ^a	Time, h	Hydrogen evolved ^b	Hydride used ^b	Hydride used for reduction ^b
Ethyl caproate	0.25	0.00	1.42	1.42
	1.0	0.00	1.75	1.75
	3.0	0.00	1.93	1.93
	6.0	0.00	1.99	1.99
Ethyl benzoate	0.25	0.00	1.67	1.67
	0.5	0.00	1.84	1.84
	1.0	0.00	1.99	1.99
Phenyl acetate	3.0	0.00	2.00	2.00
	0.25	0.00	1.43	1.43
	3.0	0.00	1.75	1.75
γ -Butyrolactone	6.0	0.00	1.90	1.90
	12.0	0.00	2.01	2.01
	0.25	0.00	1.91	1.91
	0.5	0.00	2.01	2.01
Phthalide ^c	0.25	0.00	1.24	1.24
	0.5	0.00	1.64	1.64
	1.0	0.00	1.86	1.86
	3.0	0.00	2.00	2.00
Isopropenyl acetate	0.25	0.03	1.03	1.00
	6.0	0.03	1.79	1.76
	12.0	0.03	2.00	1.97
	24.0	0.03	2.04	2.01
	48.0	0.03	2.08	2.05

^{a,b} See corresponding footnotes in Table 2, ^cSolution changed to yellow.

Table 8. Reaction of Dipyrrolidinoaluminum Hydride with Representative Epoxides in Tetrahydrofuran at 0°C

Compound ^a	Time, h	Hydrogen evolved ^b	Hydride used ^b	Hydride used for reduction ^b
1,2-Butylene oxide	0.25	0.00	0.60	0.60
	1.0	0.00	0.89	0.89
	6.0	0.00	0.97	0.97
	12.0 ^c	0.00	1.00	1.00
Cyclohexene oxide	0.25	0.03	0.62	0.59
	0.5	0.03	0.76	0.73
	3.0	0.03	0.96	0.93
	6.0	0.03	1.03	1.00
Styrene oxide ^d	0.25	0.00	0.81	0.81
	1.0	0.00	0.90	0.90
	3.0	0.00	0.94	0.94
	6.0	0.00	1.00	1.00

^{a,b} See corresponding footnotes in Table 2, ^cA mixture of 87% 2-butanol and 13% 1-butanol, ^dA mixture of 96% 1- and 4% 2-phenylethanol.

tanol. On the other hand, the reaction of styrene oxide gives a mixture of 96% 1- and 4% 2-phenylethanol. An opening of the epoxide ring is contrary to that observed with alumi-

Table 9. Reaction of Dipyrrolidinoaluminum Hydride with Representative Amides and Nitriles in Tetrahydrofuran at 0°C

Compound ^a	Time, h	Hydrogen evolved ^b	Hydride used ^b	Hydride used for reduction ^b
Caproamide	0.25	0.74	1.55	0.81
	1.0	0.93	1.85	0.92
	3.0	1.00	1.98	0.98
	6.0	1.00	2.01	1.01
	12.0	1.00	2.03	1.03
Benzamide	0.25	0.77	1.60	0.83
	1.0	0.99	1.94	0.95
	3.0	0.99	1.99	1.00
	6.0	0.99	2.00	1.01
N,N-Dimethyl-caproamide	0.25	0.00	1.58	1.58
	1.0	0.00	1.89	1.89
	6.0	0.00	1.98	1.98
	12.0	0.00	1.99	1.99
N,N-Dimethyl-benzamide	0.25	0.00	1.67	1.67
	1.0	0.00	1.92	1.92
	3.0	0.00	1.99	1.99
	6.0	0.00	2.00	2.00
Capronitrile	0.25	0.00	1.27	1.27
	1.0	0.00	1.56	1.56
	3.0	0.00	1.82	1.82
	6.0	0.00	1.99	1.99
Benzonitrile ^c	0.25	0.02	2.02	2.00
	0.5	0.02	2.02	2.00

^{a,b} See corresponding footnotes in Table 2, ^c Solution changed to yellow.

num hydride itself (100:0 and 76:24, respectively)³, but similar to that of BEAH (92:8 and 95:5, respectively)². It has long been recognized that the reduction of epoxides by aluminum hydride involves preferentially the coordination of reagent to the epoxy oxygen, followed by the hydride transfer³. In this case the hydride transfer is significantly influenced by an electrophilic component, in which there occurs a competitive transfer of hydride at the more substituted center, especially when it is benzylic in nature capable of stabilizing an electron deficiency. On the other hand, in the case of these substituted aluminum hydrides the electrophilic component seems to be less effective, but the steric requirement in the coordination sphere seems to be more influential for the hydride transfer.

We are presently engaged in a study of the reduction of such epoxides by other substituted aluminum hydrides. Consequently, a detailed discussion of the mechanisms of these reductions is best deferred until the entire subject can be discussed as a unit.

Amides and Nitriles. The reaction of primary amides liberated only 1 equiv of hydrogen readily and utilized only 1 equiv of hydride for reduction. The reaction of tertiary amides utilized 1 equiv of hydride for reduction rapidly, but the consumption of the second equivalent was relatively slow. Both capronitrile and benzonitrile utilized 2 equiv of hydride readily. It is worthwhile to note that the reaction of benzonitrile proceeded considerably more readily than that of the

Table 10. Reaction of Dipyrrolidinoaluminum Hydride with Representative Nitro Compounds and Their Derivatives in Tetrahydrofuran at 0°C

Compound ^a	Time, h	Hydrogen evolved ^b	Hydride used ^b	Hydride used for reduction ^b
1-Nitropropane	0.25	0.64	2.07	1.43
	1.0	0.83	2.68	1.85
	3.0	1.00	2.93	1.93
	6.0	1.00	3.00	2.00
	12.0	1.00	3.00	2.00
Nitrobenzene	0.25	0.99	2.52	1.53
	1.0	1.00	2.93	1.93
	3.0	1.00	2.99	1.99
	6.0	1.00	2.99	1.99
Azobenzene	0.25	0.00	1.12	1.12
	6.0	0.03	1.51	1.48
	72.0	0.03	1.75	1.72
	168.0	0.03	1.95	1.92
Azoxybenzene	0.25	0.52	1.80	1.28
	24.0	0.88	2.56	1.68
	168.0	0.90	2.88	1.98

^{a,b} See corresponding footnotes in Table 2.

aliphatic nitrile. Here again, the reactions of amides and nitriles with DPAH appeared to be quite similar to those with BEAH², except for the reaction rate. DPAH is much stronger than BEAH in its reducing potential toward these compounds. The experimental results are summarized in Table 9.

A careful examination of the rate and stoichiometry in the reaction of amides and nitriles suggests a possibility for aldehyde synthesis. We examined this possibility with use of a limiting amount of DPAH. Preliminary experiment revealed that the reactions of benzamide and N,N-dimethylbenzamide afford the corresponding aldehydes in yields of 90% and 92%, respectively, estimated by 2,4-dinitrophenylhydrazine analysis. We are exploring this transformation in greater detail.

Nitro Compounds and Their Derivatives. Unexpectedly, the reagent showed a high reactivity toward both aliphatic and aromatic nitro compounds. The reactivity of DPAH appears to be much higher than that of BEAH which is even higher than that of aluminum hydride itself. These compounds were relatively inert to aluminum hydride. Even azo- and azoxybenzenes proved to be reactive to this reagent. These results are summarized in Table 10.

Other Nitrogen Compounds. Cyclohexanone oxime liberated 1 equiv of hydrogen rapidly and utilized 1 equiv of hydride for reduction slowly, corresponding to the formation of N-hydroxycyclohexylamine. Phenyl isocyanate readily took up 2 equiv of hydride, with the third being added at a slower pace. This stoichiometry corresponds to the formation of N-methylaniline. Pyridine took up 1 equiv of hydride only for reduction, whereas 4-picoline N-oxide utilized 3 equiv of hydride of which one for hydrogen evolution and two for reduction were realized. BEAH also readily reduced cyclohexanone oxime to N-hydroxycyclohexylamine, but showed some reactivity to the other nitrogen compounds².

Table 11. Reaction of Dipyrrolidinoaluminum Hydride with Representative Other Nitrogen Compounds in Tetrahydrofuran at 0°C

Compound ^a	Time, h	Hydrogen evolved ^b	Hydride used ^b	Hydride used for reduction ^b
Cyclohexanone oxime	0.25	0.83	1.04	0.21
	1.0	0.99	1.31	0.32
	12.0	0.99	1.45	0.46
	24.0	0.99	1.82	0.83
	48.0	0.99	1.98	0.99
Phenyl isocyanate	0.25	0.00	1.20	1.20
	1.0	0.00	1.63	1.63
	3.0	0.00	1.82	1.82
	6.0	0.00	1.99	1.99
	24.0	0.00	2.22	2.22
Pyridine	48.0	0.00	2.43	2.43
	0.25	0.02	0.80	0.78
	1.0	0.02	0.87	0.85
	6.0	0.02	0.95	0.93
	12.0	0.02	1.02	1.00
4-Picoline N-oxide ^c	0.25	0.99	2.73	1.74
	1.0	1.00	2.89	1.89
	3.0	1.00	2.99	1.99
	6.0	1.00	3.00	2.00
	12.0	1.00	3.00	2.00

^{a,b}See corresponding footnotes in Table 2. ^cSolution turned to be yellowish turbid.

Table 12. Reaction of Dipyrrolidinoaluminum Hydride with Representative Sulfur Derivatives in Tetrahydrofuran at 0°C

Compound ^a	Time, h	Hydrogen evolved ^b	Hydride used ^b	Hydride used for reduction ^b
Di- <i>n</i> -butyl disulfide	0.25	0.32	0.68	0.36
	0.5	0.65	1.39	0.74
	1.0	0.87	1.82	0.95
	3.0	0.94	1.94	1.00
	6.0	1.01	2.01	1.00
Diphenyl disulfide	0.25	0.48	1.06	0.58
	0.5	0.92	1.82	0.90
	1.0	0.95	1.95	1.00
	3.0	1.00	1.99	0.99
Dimethyl sulfoxide	0.25	0.98	0.98	0.00
	3.0	1.00	1.00	0.00
Diphenyl sulfone	24.0	0.01	0.01	0.00
Methanesulfonic acid	0.25	0.98	0.98	0.00
	0.5	1.00	1.00	0.00
<i>p</i> -Toluenesulfonic acid monohydrate	0.25	2.29	2.29	0.00
	0.5	2.98	2.98	0.00
	1.0	3.00	3.00	0.00
Cyclohexyl tosylate	0.25	0.03	0.48	0.45
	1.0	0.03	0.69	0.66
	12.0	0.03	0.92	0.89
	24.0	0.03	1.02	0.99

^{a,b}See corresponding footnotes in Table 2.

These results are summarized in Table 11.

Sulfur Derivatives. The aliphatic and aromatic disulfides examined were readily reduced to the corresponding thiols within 3 h at 0°. Dimethyl sulfoxide was also rapidly reduced to dimethyl sulfide with evolution of 1 equiv of hydrogen, whereas diphenyl sulfone was absolutely stable under these reaction conditions. Interestingly, BEAH reduced all these sulfur compounds with remarkable ease. Methanesulfonic acid and *p*-toluenesulfonic acid monohydrate liberated rapidly the theoretical quantity of hydrogen. Finally, cyclohexyl tosylate was slowly reduced to utilize 1 equiv of hydride in 24 h without evolution of hydrogen. These results are summarized in Table 12.

Conclusion

The reducing properties of dipyrrolidinoaluminum hydride (DPAH) in tetrahydrofuran are now broadly characterized and compared with those of bis(diethylamino)aluminum hydride (BEAH)². The results clearly reveal that the reducing power of DPAH, an alicyclic secondary-amino derivative, is stronger than that of BEAH, an aliphatic secondary-amino derivative, but weaker than that of the parent reagent. However, the reducing action of DPAH is quite similar to that of BEAH. Especially, noteworthy is that the reagent shows a possibility for partial reduction of carboxylic acids, primary amides and tertiary amides to aldehydes. An extensive exploration is under way.

Experimental Section

All glassware used in this study was predried at 140° for several hours, assembled hot, and cooled under a stream of dry nitrogen. All reaction were carried out under a positive pressure of dry nitrogen in flasks fitted with septum-covered side arms, by using standard techniques for handling air-sensitive materials⁵. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl prior to use. Sodium aluminum hydride was obtained from Ethyl Corporation and used directly. Most of the organic compounds were commercial products of the highest purity. They were further purified by distillation or recrystallization when necessary. A Hewlett-Packard 5790A FID chromatograph equipped with a Hewlett-Packard 3390 A integrator/plotter, with use of 12 ft. × 0.125 in. column of 10% Carbowax 20 M on 100-120 mesh Supelcoport was used for GC analyses. ²⁷Al NMR spectra were recorded on a Bruker WP 80 SY spectrometer, and chemical shifts are with reference to Al(H₂O)₆³⁺. IR spectra were taken with a Perkin-Elmer 1330 spectrophotometer equipped with a sealed liquid cell.

Preparation of Solution of Sodium Aluminum Hydride (SAH) in THF. An oven-dried, 2-l, round-bottomed flask with a side arm equipped with an adaptor was attached to a mercury bubbler. The flask was flushed with dry nitrogen and then maintained under a static pressure of nitrogen. To this flask were added ca. 40 g of SAH (750 mmol) and 600 ml of THF. The slurry was stirred vigorously for 48 hrs at room temperature and then allowed to stand to permit the undissolved materials to settle. The ²⁷Al NMR spectrum of the resulting clear solution showed a clean quintet centered at δ 97 ppm (*J*_{Al-H} = 176 Hz). The concentration of SAH

in THF measured by hydrolysis was 1.2 M. The solution was used for further reactions.

Preparation of Solution of Aluminum Hydride in THF. By means of a double-ended needle and a mass cylinder, 500 ml of a 1.2 M SAH solution thus prepared was introduced into a 2-l flask, fitted with an inlet port and magnetic stirring bar and connected to a gas meter *via* a reflux condenser. The solution was cooled to 0° and precooled 600 ml of 1.0 M hydrogen chloride in diethyl ether was added slowly with vigorous stirring. There was evolved *ca.* 610 mmol of hydrogen. The mixture was permitted to stir for 1 h and then allowed to stand at 0° to permit the sodium chloride precipitate to settle. The clear supernatant solution was removed by a double-ended needle, and diethyl ether was distilled from the solution using an aspirator. The concentration of aluminum hydride in THF was 1.1 M. This solution was used for further reactions.

Preparation of Dipyrrolidinoaluminum Hydride (DPAH) in THF. To 228 ml of a 1.1 M aluminum hydride solution (250 mmol) in THF at 0°, 36.3 g of pyrrolidine (510 mmol) was added dropwise with vigorous stirring. The solution was then stirred for 6 hrs at 0°. ²⁷Al NMR spectrum of the resulting solution showed a broad singlet at δ 132 ppm relative to Al(H₂O)₆³⁺ and IR spectrum showed a stretching absorption for Al-H around 1824 cm⁻¹. The concentration of the reagent was measured by hydrolysis to be 0.80 M. The reagent was kept under a static pressure of dry nitrogen in a cold room.

General Procedure for Determination of Rates and Stoichiometry-Representative. An oven-dried, 100 ml, round-bottomed flask fitted with a rubber syringe cap on an inlet port, a magnetic stirring bar, and a bent adaptor connected to a gas buret through a reflux condenser, was immersed into an ice-water bath. To this flask were charged with 25 ml of a 0.80 M DPAH stock solution (20 mmol) and 10 ml of THF, and finally 5 ml of a 1 M solution of 1,2-butylene oxide in THF (5 mmol) was added with stirring at 0°. After 15 min, a 4.0 ml aliquot of the reaction mixture was removed and injected into a 2 N H₂SO₄-THF mixture to hydrolyze residual hydride. The hydrogen evolved amounted to 3.40 mmoles. The difference (0.60) represents the number of mmoles of hydride used per mmole of compound added. Aliquots were also removed and hydrolyzed

1.0, 6.0, and 12.0 h of reaction time. At 6.0 and 12.0 h 3.03 and 3.00 mmoles of hydrogen were evolved, respectively. These values indicate that 0.97 and 1.00 equivalents of hydride at 6.0 and 12.0 h, respectively had been utilized for reduction. Obviously the reaction was complete in 12 h (Table 8).

To determine the reaction product, 100 ml of the reaction mixture after the 12 h reaction was removed and treated with 10% H₂SO₄ to be hydrolyzed. Gas chromatographic analysis showed a mixture of 87% 2- and 13% 1-butanol in a total yield of 99%, and no starting epoxide was detected.

General Procedure for Stereoselectivity Study. The reduction of norcamphor is described as representative. To a 10 ml vial capped by rubber septum was added 2 ml of a solution of DPAH in THF (0.80 M, 1.6 mmol). The vial was maintained at 0°, and to this was added 1 ml of a 1 M solution of norcamphor in THF. The reaction mixture was stirred for 3 h at 0° and then hydrolyzed by 3 N H₂SO₄. The aqueous layer was saturated with anhydrous magnesium sulfate, and the organic layer was subjected to GC analysis to indicate the presence of 94% *endo*-norborneol. The results are summarized in Table 4.

Acknowledgements. This study was supported by NON-DIRECTED RESEARCH FUND, Korea Research Foundation, 1993, and the generous supply of sodium aluminum hydride from Ethyl Corporation (U.S.A) was gratefully acknowledged.

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